

Appl. No. : 10/696,591
Filed : October 28, 2003

REMARKS

Claims 1-33 are pending in the present application. Claim 1 has been amended to indicate that a multicomponent bismuth-containing oxide thin film selected from the group consisting of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $(\text{Bi},\text{La})_4\text{Ti}_3\text{O}_{12}$, $\text{SrBi}_2\text{Ta}_2\text{O}_9$, and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ is deposited. Support can be found, for example, in original Claim 16. Claim 10 has been amended to indicate that a multicomponent oxide thin film is deposited. Support can be found in original Claim 14. Claims 12, 15, 18, 17 and 25 have been amended in view of the changes to Claim 10. No new matter is added by these amendments.

Objections to the Specification

The title of the application was objected to as not being descriptive. As suggested by the Examiner, Applicants have amended the title to "Process for producing bismuth-containing oxide films." Thus, Applicants submit that this objection can be withdrawn.

Claim Rejections Under 35 U.S.C. §112

Claims 5, 16 and 33 were rejected under 35 U.S.C. first and second paragraphs, with the Examiner finding that in Claim 16 the formula $(\text{Bi},\text{La})_4\text{Ti}_3\text{O}_{12}$ omits the stoichiometric subscript on Bi and thus fails to distinctly claim the subject matter and prevents one of skill in the art from making and using the claimed invention. Applicants disagree and submit that formula is well-known in the art as the ferroelectric material BLT. As an example, Applicants provide a courtesy copy of Hwan and Chang (J. Korean Phys. Soc. 41(1):139-143 (2002)).

As $(\text{Bi},\text{La})_4\text{Ti}_3\text{O}_{12}$ is well known in the art, Applicants submit that the rejections under 35 U.S.C. §112 should be withdrawn. Applicants note that the reason for the inclusion of Claim 5 was not clear from the rejection, as the claim was not explicitly addressed and does not recite the formula objected to by the Examiner.

Claim Rejections Under 35 U.S.C. §102

Claims 1-3, 6-7, 10, 22 and 24 were rejected under 35 U.S.C. §102(b) as being anticipated by Gordon (WO 02/27063). The Examiner found that Gordon discloses a process for producing a bismuth-containing oxide thin film by ALD on page 1, lines 1-3 and 23-24. In fact,

Gordon generally refers to the deposition of metal oxides, silicates or metal phosphates or silicon dioxide by ALD. The only reference to bismuth is the recitation of a single bismuth compound in Table 1, a listing of almost 150 volatile metal or metalloid amides. There is no direct reference to the deposition of a bismuth-containing oxide film by ALD, no teaching of the particular reactions conditions that could be used for depositing bismuth-oxide films, and no suggestion of how the disclosed process could be adapted to deposit bismuth-oxide films.

Nevertheless, Applicants have amended Claim 1 to indicate that the bismuth-containing oxide thin film is selected from the group consisting of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $(\text{Bi},\text{La})_4\text{Ti}_3\text{O}_{12}$, $\text{SrBi}_2\text{Ta}_2\text{O}_9$, and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$. As Gordon has no teaching of these films, the rejection of Claim 1 and the claims that depend therefrom should be withdrawn.

Similarly, Claim 10 has been amended to recite that a bismuth-containing thin film is a multicomponent oxide thin film, as previously recited in Claim 14. As Gordon does not teach or suggest a multicomponent oxide thin film comprising bismuth, Applicants request withdrawal of the rejection of Claims 10, 22 and 24 as well.

Claim Rejections Under 35 U.S.C. §103

The Examiner rejected the majority of the claims under 35 U.S.C. §103 on a variety of grounds. Without acquiescing in the rejections, Applicants have amended Claims 1 and 10 as discussed above to recite multicomponent oxides. These amendments obviate a number of the rejections. The relevant remaining rejections rely on the combination of Gordon and Hintermaier (U.S. 6,177,135).

For example, with respect to Claims 5, 13, 16 and 33, the Examiner found that it would have been obvious to modify Gordon to include multicomponent or ternary oxide films as described in Hintermaier in order to provide oxide films having ferroelectric properties. Similarly, with respect to Claims 11, 14, 19-20 and 26-27 the Examiner found that while Gordon does not explicitly disclose combining a bismuth compound with a silylamido ligand with at least a second metal precursor to form a bismuth-containing multicomponent oxide, Hintermaier teaches forming Bi-containing multicomponents oxides in order to make oxide films with ferromagnetic properties. Also, with respect to Claims 12 and 15 the Examiner found that it would have been obvious to include Sr, Ta and/or Ti precursors as a second metal source in the

ALD process of Gordon because “to do so would have reasonably been expected to provide the desirable ferroelectric Bi-containing multicomponent oxides useful in non-volatile memory devices [taught in Hintermaier].”

Applicants respectfully submit that there is no suggestion to modify Gordon to produce the multicomponent bismuth-containing films described in Hintermaier and that, even if such a suggestion did exist, there is no teaching of how to modify Gordon to deposit such multicomponent films and thus no reasonable expectation of success.

ALD utilizes self-saturating surface reactions and thus depends upon the particular nature of the precursors used and selection of particular reaction conditions. Importantly, there is no universal set of conditions under which ALD will work. Rather, particular deposition recipes must be developed for each type of film to be deposited. Not all precursors are suitable for ALD, and the precursors are chosen based on the particular context. Thus, even if there is a teaching in the general art of the desirability of depositing a particular film type, such a suggestion does not render obvious the particular ALD methods that must be developed to deposit that film.

As mentioned above, Gordon has no explicit teaching of deposition of a bismuth-containing thin film and recites only a single bismuth precursor. Hintermaier teaches only CVD processes for depositing bismuth-containing thin films, *not ALD*. CVD processes work on very different principles from ALD and are not interchangeable with ALD processes. See, for example, the Abstract of Hintermaier, which teaches that the CVD reactions are based on *decomposition* of precursors at the substrate surface. In contrast, ALD conditions are chosen that *avoid decomposition* and achieve the self-limiting reactions that are the trademark of ALD. Thus, while Hintermaier may suggest various types of bismuth-containing films with desirable properties, it does not provide any teaching about how such films can be deposited by ALD.

In addition, Gordon does not have any particular teaching about the desirability of depositing bismuth-containing multicomponent oxide films by ALD and Hintermaier does not suggest that the films they deposit by CVD are lacking in some way such that they would benefit from deposition by ALD. As films are grown monolayer by monolayer using ALD processes and thus have reduced throughput and a corresponding increased cost, without some particular reason to utilize ALD the skilled artisan would select a process with a higher throughput, such as CVD.

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In the absence of any teaching or suggestion in either reference of any advantage to depositing bismuth-containing multicomponent oxide thin films by ALD, Applicants respectfully submit that the requisite motivation for the combination has not been provided. Further, the teaching of multicomponent bismuth films in Hintermaier is at most an invitation to *try* to deposit such films by ALD. As the Examiner is well aware, obvious to try is not the standard for obviousness. Rather, there must be an expectation of success in the combination. Here, there is no teaching of any ALD process for depositing bismuth-containing oxides by ALD, much less multicomponent bismuth-containing oxides. Thus, Applicants submit that there can be no expectation of success.

In view of the above, as each of independent Claims 1, 10, 26 recites the deposition of a multicomponent bismuth-containing thin film by ALD, Applicants submit that a prima facie case of obviousness has not been established and request the withdrawal of the rejections under 35 U.S.C. §103.

Finally, Applicants note that Claims 17 and 18 were also rejected over the combination of Gordon and Hintermaier, with the Examiner finding that while Gordon does not specify a reaction temperature on the substrate, Hintermaier teaches a substrate temperature of below 400°C “in order to control the decomposition mechanism on the substrate.” Again, Applicants submit that Hintermaier is a CVD reference and thus its teachings are not directly applicable to an ALD process.

In a CVD process, reactant decomposition is utilized in order to achieve deposition. In contrast, in ALD decomposition is necessarily avoided in order to achieve self-limiting surface reactions. The teaching of a temperature range that is useful to provide controlled decomposition of precursors provides no teaching or suggestion of a temperature range that *avoids decomposition entirely*, much less of a temperature range that is suitable for ALD (avoid decomposition and also provides sufficient reactivity and avoids condensation of reactants). Thus, the skilled artisan would not look to the teachings of Hintermaier for teaching of a temperature that is useful for depositing bismuth-containing oxides by ALD and Applicants request withdrawal of this rejection of Claims 17 and 18.

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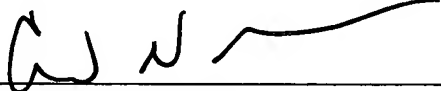
Conclusion

For the reasons presented above, Applicants submit that the present application is in conditions for allowance and respectfully request the same. If any issues remain, the Examiner is cordially invited to contact Applicants' representative at the number provided below in order to resolve such issues promptly.

Respectfully submitted,

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Properties of (Bi,La)Ti₃O₁₂ Thin Films Grown by Using the Sol-Gel Method and for Nonvolatile Memories

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Bi_{3.7}La_{0.75}Ti₃O₁₂ (BLT) ferroelectric thin films were prepared on Pt/Ti/SiO₂/Si substrates by using the sol-gel method. The as-coated films were crystallized by post-annealing at 650 °C and 750 °C for 30 min. The BLT thin films exhibited typical bismuth-layered perovskite structures, and the crystalline quality was improved by post-annealing in an air ambient. The auger electron spectroscopy (AES) depth profiles indicated that no remarkable interfacial reaction layers existed between the BLT film and the lower electrode. The dielectric constant and the dissipation factor of the BLT films post-annealed at 750 °C were about 402 and 0.04 at 5 kHz, respectively. The leakage current density of the BLT films annealed at 650 °C was found to be 5×10^{-7} A/cm² at 3 V. The BLT film annealed at 650 °C exhibited ferroelectric properties with a remanent polarization, 2Pr (Pr⁺-Pr⁻), of 32.5 μC/cm² and showed no degradation after 10¹⁰ polarization switching cycles under ±5 V bipolar pulse, indicating good resistance to fatigue.

PACS numbers: 70.77

Keywords: (Bi,La)Ti₃O₁₂ (BLT), Thin film, Sol-gel, Ferroelectric, Monvolatile memory

I. INTRODUCTION

As modern electronic devices, such as mobile phones and notebook computers, become popular, the demand for nonvolatile memory devices has increased. Ferroelectric thin films have attracted much attention for applications in nonvolatile ferroelectric random access memories (NVFeRAM) from the view points of high speed operation, low power consumption, and large scale integration [1,2]. There are two kinds of ferroelectric nonvolatile memory devices. One is a memory device with one transistor and one ferroelectric storage capacitor, and the other is the metal-ferroelectric-semiconductor field effect transistor (MFS-FET). Generally, the ferroelectric gate FET is recognized as a better memory device due to its nondestructive read-out capability and large-scale integration.

Until recently, some fabrication methods, such as the sol-gel method, metalorganic decomposition (MOD), RF magnetron sputtering, and pulsed laser deposition (PLD), have been developed and demonstrated [3-6]. Among these various techniques, the sol-gel method provides a high-quality film, as well as rapid and inexpensive processing, on a large-area substrate. This method is also compatible with many semiconductor fabrication technologies. Pb-free ferroelectric materials, such as SrBi₂Ta₂O₉ (SBT), (Bi,La)Ti₃O₁₂ (BLT), SrBi₄Ti₃O₁₅,

and SrBi₂Nb₂O₉ (SBN), are known to be promising materials [7-10] for NVFeRAM applications due to their good fatigue properties, low leakage currents, and high remanent polarization [11-15]. In particular, BLT is one of the most promising candidates for NVFeRAM.

For the feasibility study of NVFeRAM applications, it is essential to characterize the various properties of BLT films systematically. In this research, BLT thin films were prepared on Pt/Ti/SiO₂/Si substrates by using the sol-gel method, and the dependences of the crystallinity and the electrical properties on the post-annealing temperatures were investigated.

II. EXPERIMENTAL PROCEDURE

BLT thin films were coated on Pt/Ti/SiO₂/Si substrates by using the sol-gel method. The BLT sol-gel solution was synthesized using a lanthanum acetate hydrate, bismuth 2-ethylhexanoate, and titanium isopropoxide with MEOH (methoxyethanol) solution. The excessive Bi component, 20 mole%, was added to compensate for its volatility during the post-annealing procedure. The sol-gel solution was spin-coated onto the substrate in two steps, with a rotational speed of 2000 rpm for 5 seconds and then 4000 rpm for 25 seconds, to obtain a uniform coating on the film surface. After spin coating, the films were baked in an oven at 170 °C to remove residual solvent. The coating and drying cycles

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Table 1. Atomic molar ratios of the as-coated BLT films and the films annealed at 650 °C and 750 °C.

Annealing Temp.(°C)	Bi	La	Ti
As-coated	3.70	0.75	3.05
650	3.40	0.60	3.03
750	3.27	0.62	3.08

were repeated 3 times. The film thickness was about 1300 Å. The as-coated films were pre-annealed at 450 °C for 30 seconds in an O₂ atmosphere in a rapid thermal annealing (RTA) system. For crystallization of BLT films, the post-annealing was conducted at temperatures of 650 °C and 750 °C for 30 min under an air ambient. For the electrical measurements, an Al top electrode was deposited onto the BLT film layer by using thermal evaporation through a metal shadow mask to form ferroelectric capacitors. Annealing at 400 °C in a N₂ ambient was carried out for 10 min in the furnace in order to obtain good ohmic contact between the Al top electrode and the BLT film.

The crystalline structures of the films were analyzed using X-ray diffractometer (XRD). The surface and cross-sectional morphologies were examined using scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. The chemical compositions and impurity contents of the films were examined by using auger electron spectroscopy (AES) and wave dispersive spectrometry (WDS), respectively. The P-E hysteresis and fatigue properties were measured under an applied bias of ± 5 V by using an RT66A measurement system. The electrical properties, such as the leakage current and the dielectric constant (ϵ_r) were determined by using HP4145B and HP4192A analyzers.

III. RESULTS AND DISCUSSION

To investigate the atomic molar ratios of BLT films, we used WDS to analyze the films. The atomic ratio of the as-coated film was found to be non-stoichiometric with the molar formula Bi_{3.7}La_{0.75}Ti₃O₁₂. The Bi content decreased by about 12 mole% when the annealing temperature was increased to 750 °C, which increased the volatility of the Bi component during the post-annealing. Table 1 shows the atomic molar ratios of the as-grown BLT films and the BLT films annealed at 650 °C and 750 °C.

Figure 1 shows the XRD patterns of the (a) as-coated BLT film and the films annealed at (b) 650 °C and (c) 750 °C. The films annealed at temperatures above 650 °C exhibited a typical bismuth-layered perovskite structure. The peak intensities were increased and the full width at half maximum (FWHM) value of the (006) peak was decreased from 0.31° to 0.27° by increasing the annealing temperature from 650 °C to 750 °C, suggesting an im-

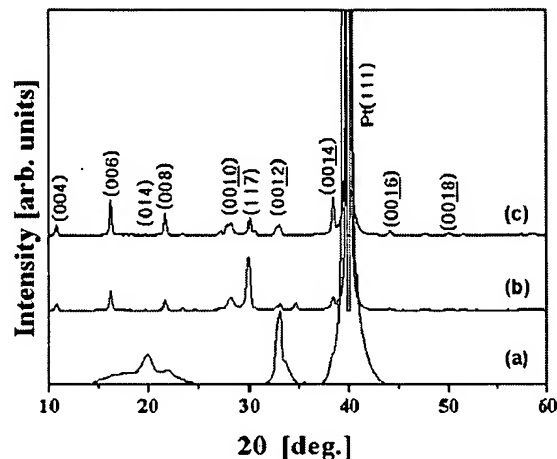


Fig. 1. XRD patterns of (a) the as-coated BLT film and of the films annealed at (b) 650 °C and (c) 750 °C.

provement in the crystallinity. On the other hand, the as-coated films showed mixed crystalline structures with amorphous and partial crystalline phases because of the low-temperature pre-annealing using an RTA process at 450 °C.

The depth profiles of the films were measured to confirm the interfacial reactions between the film and the lower electrode. Figure 2 represents the AES depth pro-

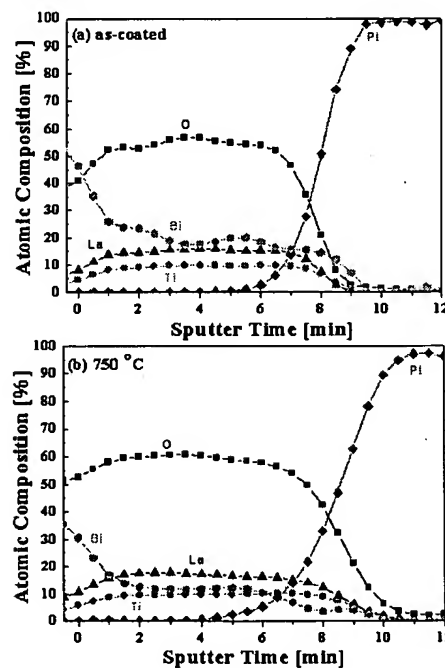


Fig. 2. AES depth profiles of (a) the as-coated BLT film and (b) the film annealed at 750 °C.

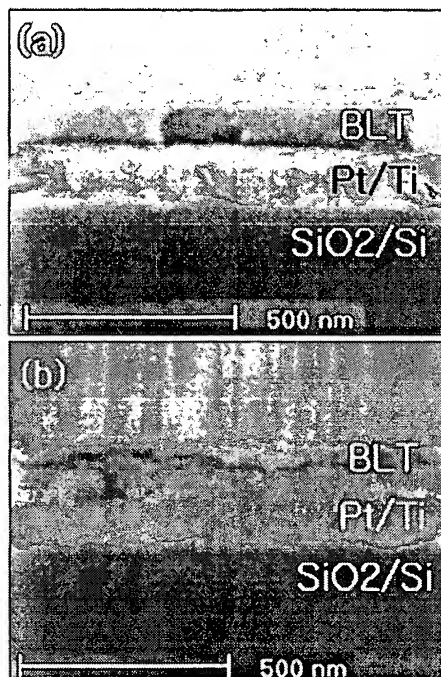


Fig. 3. SEM cross-sectional micrographs of (a) the as-coated BLT film and (b) the sample annealed at 750 °C.

files of the (a) as-coated BLT film on a Pt/Ti/SiO₂/Si substrate and (b) the sample annealed at 750 °C. The AES results show that BLT/Pt interface is stable. No remarkable interfacial reactions were found in either sample.

The SEM cross-sectional micrographs of the (a) as-coated BLT film and (b) the sample annealed at 750 °C are shown in Fig. 3. From the cross-sectional views, we found that the BLT film thickness was about 1300 Å. Also, grains with flat shapes were seen on the cross-sectional surface of the BLT film which was annealed at 750 °C.

Figure 4 shows the SEM surface micrographs of the (a) as-coated BLT film and the films annealed at (b) 650 °C and (c) 750 °C. The surface morphology of the as-coated film was found to be relatively smooth. The grain size was increased by increasing the post-annealing temperature.

Figure 5 shows the AFM images of the (a) as-coated BLT film and the films annealed at (b) 650 °C and (c) 750 °C. The AFM images indicate that the surface roughness was affected by the annealing temperatures. The R_{rms} value of the as-coated film was 3.82 Å with a rather smooth surface whereas the R_{rms} value of the BLT film annealed at 750 °C was 12.9 Å, showing a rough film surface. These results are consistent with the SEM micrographs in Fig. 4.

Figure 6 shows the P-E hysteresis loops of the (a) as-coated BLT film and the samples annealed at (b) 650

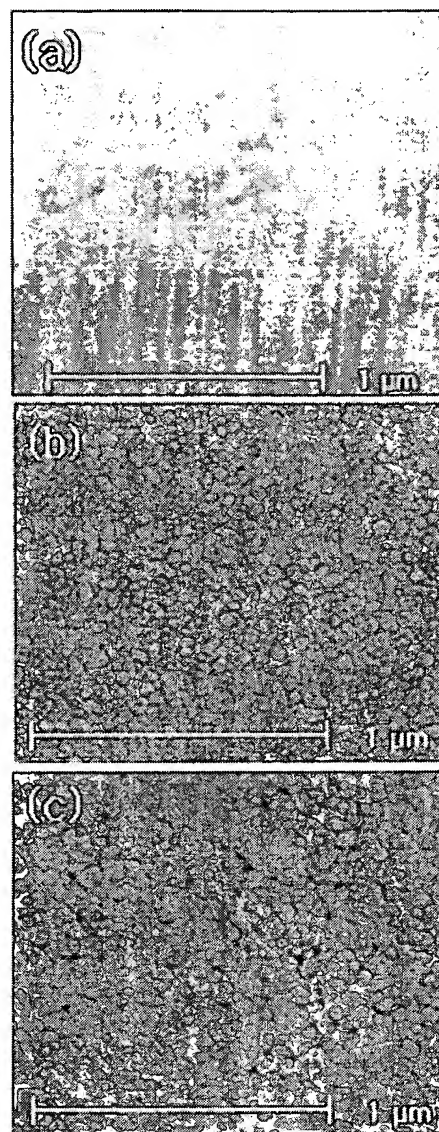


Fig. 4. SEM surfacial micrographs of (a) the as-coated BLT film and of the films annealed at (b) 650 °C and (c) 750 °C.

°C and (c) 750 °C. The remanent polarization depended strongly on the annealing temperature. The hysteresis loop of the as-coated film showed paraelectric properties which were changed to ferroelectric properties by annealing at temperatures above 650 °C. The calculated values of the remanent polarization ($2P_r = P_r^+ - P_r^-$) and the coercive field (E_c) were 32.5 $\mu\text{C}/\text{cm}^2$ and 114 kV/cm, respectively.

To investigate the fatigue properties, we applied ± 5 -V bipolar switching pulses to the BLT films. We found that the BLT films showed no degradation in polarization after 10^{10} switching cycles, which indicated that BLT

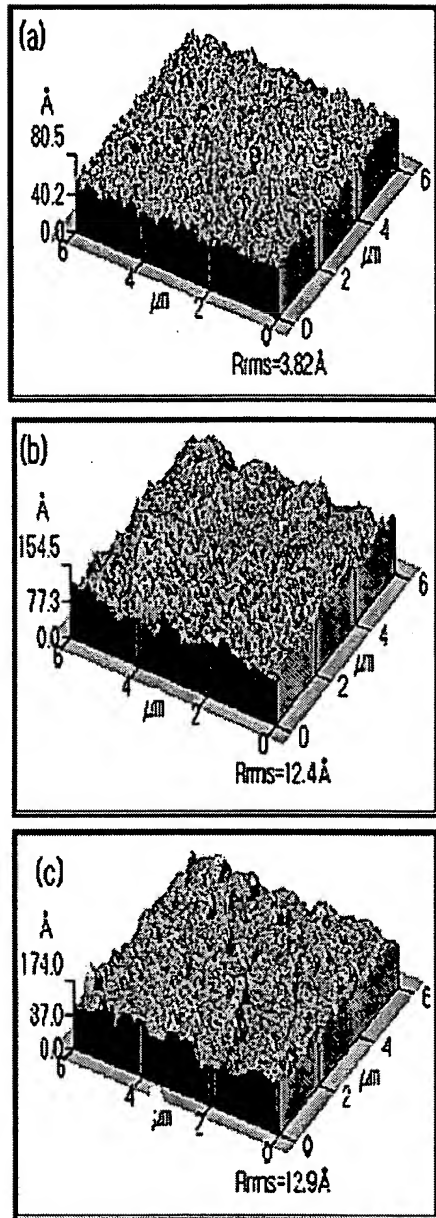


Fig. 5. AFM images of (a) the as-coated BLT film and of the films annealed at (b) 650 °C and (c) 750 °C.

films have good resistance to fatigue.

Figure 7 shows the dielectric constant (ϵ_r) and the dissipation factor ($\tan\delta$) for BLT films annealed at various temperatures as functions of the frequency. The dielectric constant of the as-coated film was about 305 and was increased to 402 by increasing the annealing temperature to 750 °C. This may be related to an increase in the grain size and a decrease in the grain boundary layers, which have a low dielectric constant [16]. The

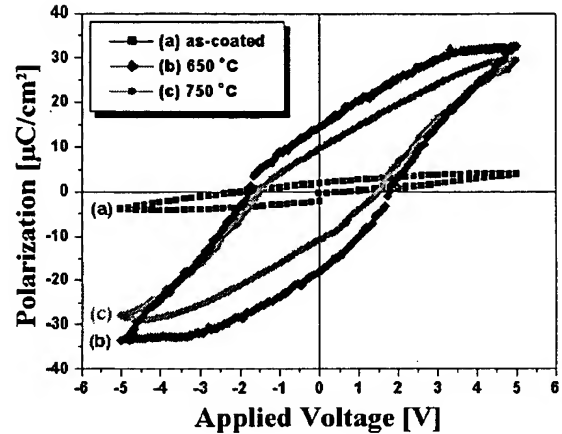


Fig. 6. P-E hysteresis loops of (a) the as-coated BLT film and of the films annealed at (b) 650 °C and (c) 750 °C.

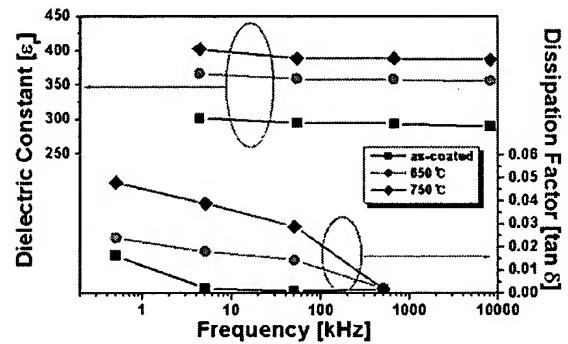


Fig. 7. Dielectric constants (ϵ_r) and dissipation factors ($\tan\delta$) of the various BLT films as functions of the frequency.

dissipation factor of the as-coated film was about 0.016 at 0.5 kHz and decreased to 0.002 at 0.5 MHz for the film annealed at 750 °C.

The current densities of the BLT films annealed at (a) 650 °C and (b) 750 °C as functions of the applied voltage are shown in Fig. 8. The current density of the BLT film annealed at 650 °C was about 5×10^{-7} A/cm². It was also found that the film post-annealed at 750 °C had a leakage current slightly larger than that of the sample post-annealed at 650 °C. That result can be explained by the grain growth caused by the increased post-annealing temperature, as seen in the SEM morphologies in Fig. 4.

IV. CONCLUSIONS

$\text{Bi}_{3.7}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT) ferroelectric thin films were prepared on Pt/Ti/SiO₂/Si substrates by using the sol-gel method. The films were then crystallized by post-annealing at temperatures of 650 °C and 750 °C under an air ambient. The BLT thin films exhibited typi-

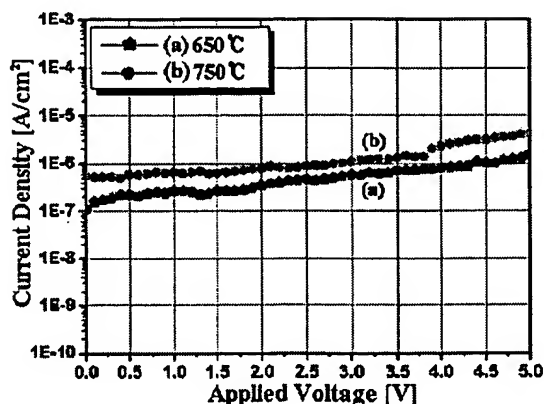


Fig. 8. Current-voltage curves of the BLT films annealed at (a) 650 °C and (b) 750 °C as functions of the applied voltage.

cal bismuth-layered perovskite structures, and the crystalline quality was improved by the post-annealing. The AES depth profiles indicated that no remarkable interfacial reaction layers existed between the BLT film and the lower electrode. The dielectric constant and the dissipation factor of the films annealed at 750 °C were about 402 and 0.04 at 5 kHz, respectively. The dielectric constant was increased by increasing annealing temperatures; that behavior might have resulted from the increased grain size. The remanent polarization ($2P_r = P_r^+ - P_r^-$) and the coercive field of the film annealed at 650 °C were 32.5 $\mu\text{C}/\text{cm}^2$ and 114 kV/cm, respectively. The BLT film annealed at 650 °C showed no degradation after 10^{10} polarization switching cycles, indicating a good resistance to fatigue.

ACKNOWLEDGMENTS

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